Diffraction Basics, Part 2

Introduction

The material in the previous section is concerned primarily with the origin of diffraction peaks and the application of the reciprocal lattice to the interpretation of peak positions. This section is concerned primarily with the other aspect of X-ray diffraction data – the intensity of the diffraction peaks and how variations in those intensities are related to the chemistry and arrangement the atoms in the crystal structure of the analyzed material. This section concludes the basic theory of X-ray diffraction. Although the balance of the course will be concerned with use of the powder diffractometer to acquire and interpret experimental data, basic understanding of the theory is essential in any successful practical application.

Material in this section is taken from a variety of sources, primarily Jenkins and Snyder (1996) and Nuffield (1966), supplemented by notes from a short course on powder diffraction taken by the author at the International Center for Diffraction Data (ICDD) during the summer of 2002.

Intensity Variations in X-ray Powder Data

Overview

The position of diffraction peaks and the d-spacings that they represent provide information about the location of lattice planes in the crystal structure. Each peak measures a d-spacing that represents a family of lattice planes. Each peak also has an intensity which differs from other peaks in the pattern and reflects the relative strength of the diffraction. In a diffraction pattern, the strongest peak is, by convention, assigned an intensity value of 100, and other peaks are scaled relative to that value. Although peak height may be used as a qualitative measure of relative intensity, the most accurate measure of intensity relationships in a pattern is the area (minus background) under the peaks.

Variations in measured intensity are related chiefly to variations in the scattering intensity of the components of the crystal structure – the atoms, molecules – and their arrangement in the lattice. Some of the most dramatic variations are related to interference between diffractions produced in the lattice; these can produce systematic extinctions or greatly reduced intensities of peaks from certain lattice planes.

Scattering

In diffraction, we are concerned with coherent scattering, that is, the scattering in which the incident X-rays interact with a target atom, exciting it and causing it to be a secondary point source of X-rays of the same energy (wavelength). The intensity of that scattering is the result of a variety of processes the sum of which results in scattering which "looks" like it comes from the atom as a whole.

Scattering by an Electron

An electron will oscillate in phase with an x-ray beam according to the following equation (called the Thompson equation after J.J. Thompson who demonstrated the relationship in 1906):

$$I = \frac{I_O}{r^2}\left[\frac{e^2}{m_e c^2}\right]^2 \frac{1+\cos^2(2\theta)}{2}$$

where I_0 is the intensity of the incident beam; e the charge on the electron; m_e the mass of the electron; c the speed of light; and r the distance from the scattering electron to the detector (with the r^2 term in the denominator expressing the inverse square law). Clearly (by the second term) the scattered energy from a single electron is quite low. Third term, involving the cosine function, is called the *polarization factor* because it indicates that the incoming non-polarized x-ray is polarized by the scattering process, resulting in a directional variation in the scattered intensity.

Scattering by an Atom

Scattering by an atom is essentially the sum of the scattering of the electron "cloud" around the nucleus.
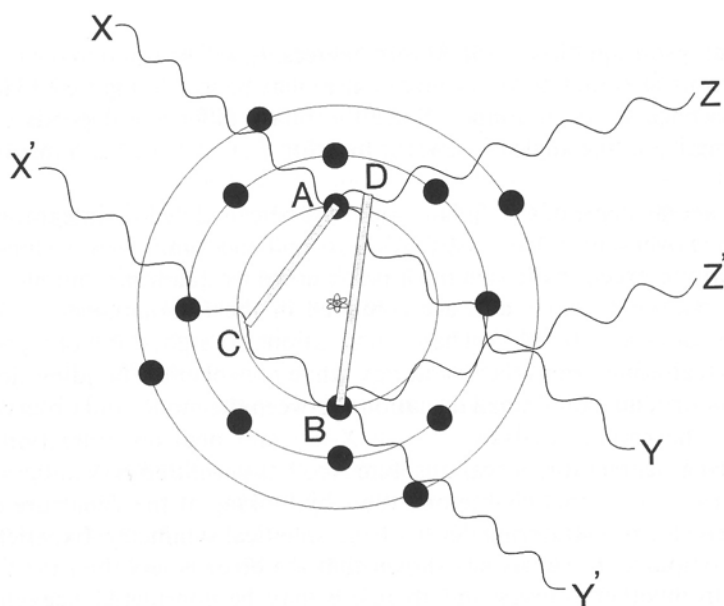
The process is illustrated in the simplified diagram at left (Fig. 3.12 from Jenkins and Snyder, 1996). Scattering from each electron follows the Thompson equation. Because of the distance between electrons scattering within the atom and the fact that the x-ray wavelength is of the same order as the atomic dimensions, there will be path differences between the scattered waves. These differences will always be less than one wavelength, so the interference will always be partially destructive.

Figure 3.12. The scattering of X-rays from a real atom extended in space.

This phenomenon is called the *atomic scattering factor*, described by the quantity f_0. This function is normalized in units of the amount of scattering occurring from a single electron in the Thompson equation. At zero degrees, f_0 will be equal to the number of electrons surrounding the atom or ion. At higher scattering angles, the factor will be less. f_0 is generally expressed as a function of $\sin\theta$ and λ as shown below for Cu (Fig. 3.13 from Jenkins and Snyder, 1996).

The actual shape of the f_0 function is calculated by integrating scattering over the electron distribution around an atom. These calculations involve very complex quantum approximation methods and have been compiled in the International Tables for Crystallography (Vol. 3). Atomic scattering factors are usually given either in tables as a function of $(\sin\theta)/\lambda$ or as coefficients of polynomials fit to curves like those shown in Figure 3.15 (from Nuffield, 1966).

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Anomalous Scattering

Anomalous scattering or *anomalous dispersion* occurs when the incident x-ray energy is sufficient to cause photoelectric x-ray production in a target atom. The process is called fluorescence. This phenomenon is responsible for "absorption edge" phenomenon that occurs with certain elements when interacting with particular wavelength x-rays. In this process a characteristic x-ray photon is produced in the target; subsequent interaction produces coherent x-rays which are slightly out of phase with other coherently scattered x-rays. The net result is a reduction of the scattered intensity from the element.
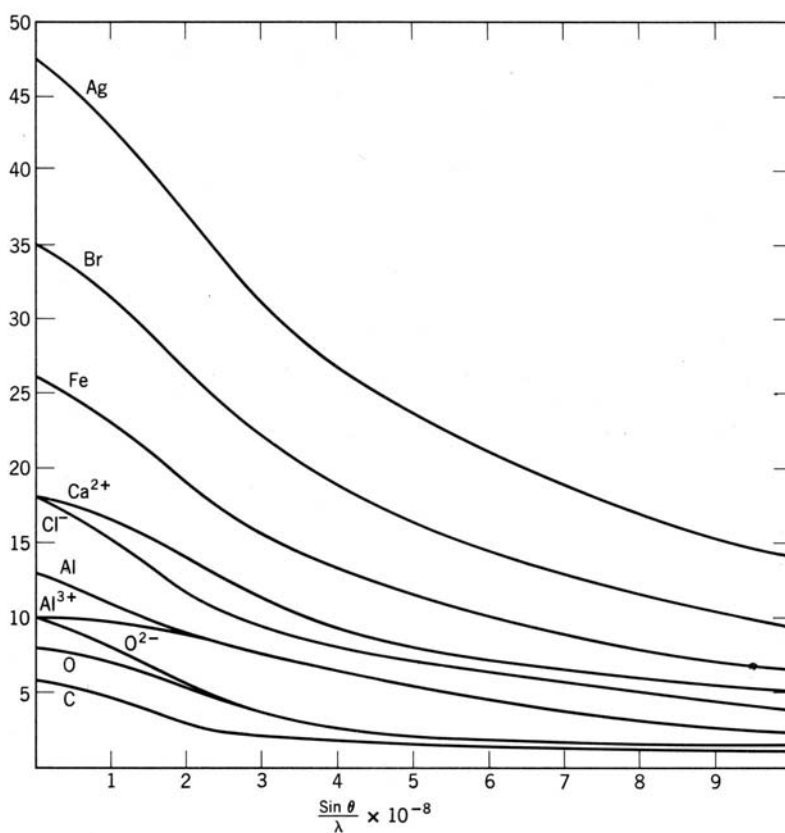

Fig. 3-15. Diffracting power of a few common atoms and ions (after C. W. Bunn, *Chemical Crystallography*, Oxford University Press, 1945).

This "absorption edge" phenomenon is responsible for reduction of diffracted intensity for materials containing certain elements. The table below lists the common x-ray source anodes and the elements for which this absorption effect occurs.

Target (Anode) Element	λ of $K_{\alpha 1}$ in Angstroms	Elements with strong fluorescence
Cr	2.2909	Ti, Sc, Ca
Fe	1.9373	Cr, V, Ti
Co	1.7902	Mn, Cr, V
Cu	1.5418	Co, Fe, Mn
Mo	0.7107	Y, Sr, Rb

Quantitatively, the calculation of the correction to f_0 involves a real ($\Delta f'$) and imaginary ($\Delta f''$) term. The effective scattering will be:

$$|f|^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$$

(Material in this document is borrowed from many sources; all original material is ©2007 by James R. Connolly)

Values for the coefficients are tabulated in the International Tables for Crystallography. In actual practice, these corrections are only significant for those elements for which absorption edge fluorescence effects are significant.

Thermal Motion

The thermal vibrational amplitude of the atom will have an effect on x-ray scattering. The effective scattering is described by the following relationship:

$$ f = f_0 \exp\left[-\frac{B \sin^2 \theta}{\lambda^2} \right] $$

B is the Debye-Waller temperature factor and is defined as: $B = 8\pi^2 U^2$. U^2 is the mean-square amplitude of vibration of an atom, and is directly related to the thermal energy (kT) available with other terms related to atomic mass and the strength of interatomic bonds. Qualitatively, as T increases (other factors constant), B will increase. When B = 0, the scattering will follow the Thompson equation. As B increases, scattering will be reduced in amplitude. This relationship is shown in Fig 3.14 (Jenkins and Snyder, 1996) below:
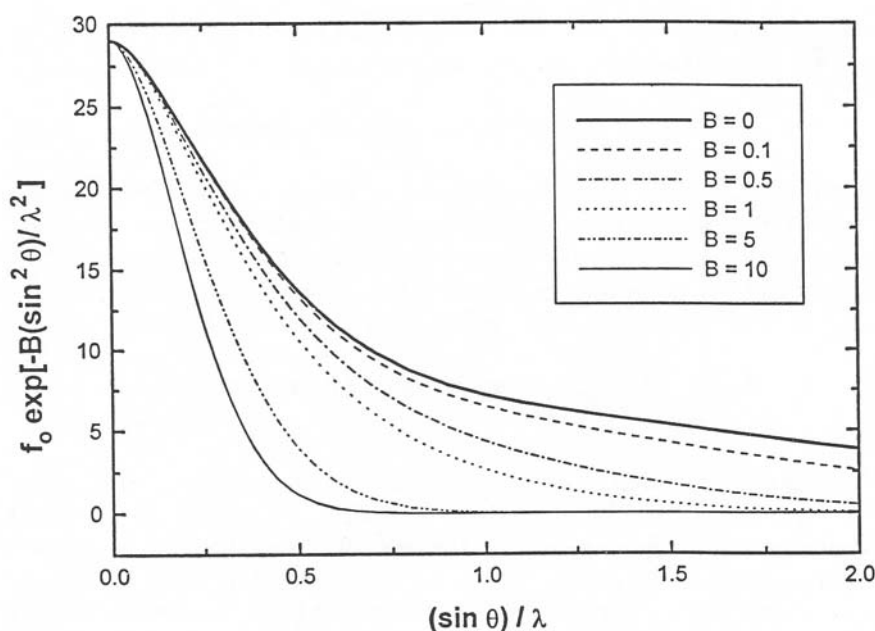

Figure 3.14. The effect of atomic thermal motion on the copper scattering factor.

Unlike other scattering factors, the computation of the temperature factor is extremely complex, based on tensor relationships on which there is not widespread general agreement.

Scattering of X-Rays by a Unit Cell: The Structure Factor

The unit cells of most crystalline substances contain a several different elements whose atoms are arranged in a complex motif defined by a variety of point group symmetry elements and replicated by translational elements into a three-dimensional lattice array.

The structure may be thought of as repeating planar arrays of atoms. The geometry of peaks is related fundamentally to positions of those atoms with little regard to what those atoms are. Intensity, on the other hand, is definitely related to the composition because the intensity of

scattering is related to atomic scattering. The structure factor is a means of grouping the atoms in the unit cell into planar elements, developing the diffraction intensities from each of those elements and integrating the results into the total diffraction intensity from each d_{hkl} plane in the structure.

We can define *F(hkl)* as the structure factor for the (hkl) plane. A particular (hkl) plane is the result of reflections from a series of parallel atomic planes where f_1, f_2, f_3, etc. are the amplitudes of the respective atomic planes. The phase factors (ϕ_N) are the repeat distances between the atomic planes measured from a common origin. The general expression for the structure factor for a (hkl) is:

$$F(hkl) = \sum_N (f_N, \phi_N)$$

where f_N is the *f* value of the Nth kind of atom in the cell, and ϕ_N is its phase factor. This relationship is most easily visualized as an addition of vectors as shown in the diagram below (Fig. 3-16 from Nuffield, 1966).
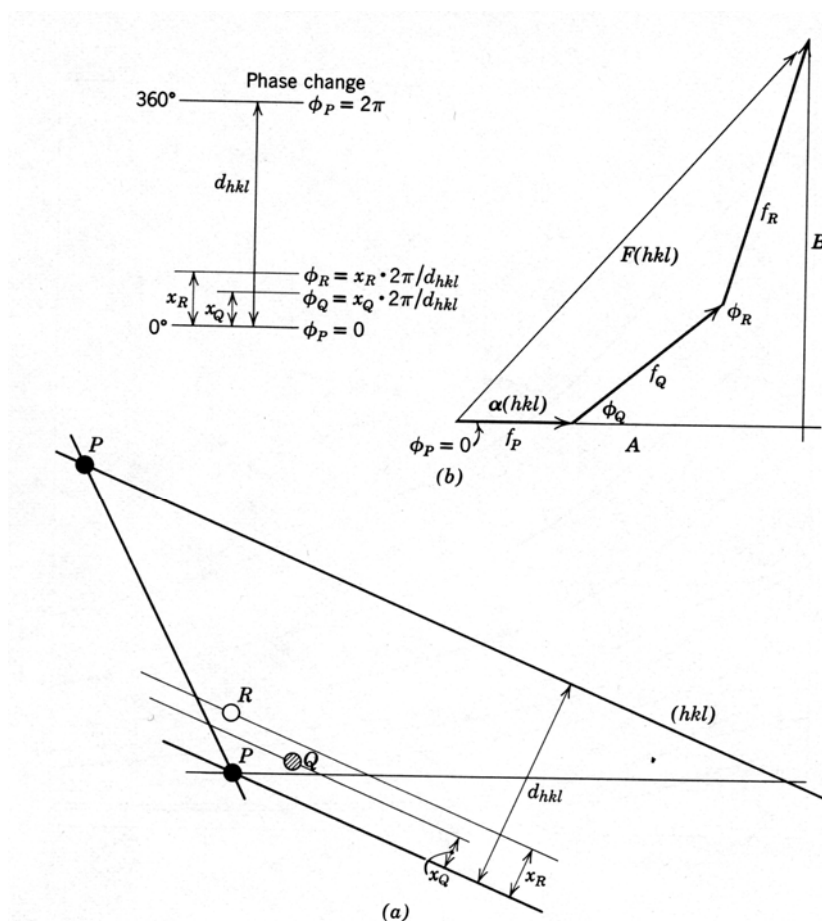

Fig. 3-16. Vector representation of waves with different amplitudes and phases.

In this diagram, three different atoms, P, Q and R are arranged in a two-dimensional lattice repeating at interval d_{hkl} (Fig. 3-16a). Nuffield presents the structure factor in slightly different terms as shown by the expressions for ϕ_P, ϕ_Q, and ϕ_R.

F(hkl) is shown as the sum of the component vectors. Though the mathematics of the actual calculations in three dimensions involve complex tensor operations, it is conceptually useful to understand the structure factor as a summation of directional vectors.

For a more rigorous treatment of the structure factor, the reader is referred to Nuffield (1966), Jenkins and Snyder (1996) or any other text on x-ray diffraction.

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Extinction

In certain lattice types, the arrangement and spacing of lattice planes produces diffractions from certain classes of planes in the structure that are always exactly 180° out of phase producing a phenomenon called *extinction*. In these cases, certain classes of reflections from valid lattice planes will not produce visible diffractions. For example, for a body-centered cubic cell, for each atom located at x, y, z there will be an identical atom located at x+½, y+½, z+½. The structure factor $\mathbf{F}_{hkl}$ is represented by the following equation.

$$\mathbf{F}_{hkl} = \left(\sum_{j=1}^{m/2} f_n \exp\left[2\pi i(hx_j + ky_j + lz_j)\right] \right) + \left(\sum_{n=1}^{m/2} f_n \exp\left[2\pi i(hx_j + \frac{h}{2} + ky_j + \frac{k}{2} + lz_j + \frac{l}{2}) \right] \right)$$

While complicated, it is noted that if $h + k + l$ is even, then the second term will contain an integer, n, in it. An integral number of 2π's will have no effect on the value of this term and the equation reduces to:

$$\mathbf{F}_{hkl} = \sum_{j=1}^{m/2} 2 f_n \exp\left[2\pi i(hx_j + ky_j + lz_j)\right]$$

If $h + k + l$ is odd, however, the second term will contain an integer with a $2\pi(n/2)$ term; here n is any integer and represents a full rotation of the scattering vector. This causes the second term to be negative, and the net result is there is no diffracted intensity (since $\mathbf{F}_{hkl} = 0$). This condition is called a *systematic extinction*. The table below lists the systematic extinction conditions due to translational symmetry elements[1]:

Symmetry	Extinction Conditions
P	none
C	hkl; h + k = odd
B	hkl; h + l = odd
A	hkl; k + l = odd
I	hkl; h + k + l = odd
F	hkl; h, k, l mixed even and odd
$2_1 \parallel b$	0k0: k = odd
$c \perp b$	h0l: l = odd

Other systematic extinctions can occur as a consequence of rotational operations (screw axes and glide planes).

Extinctions can also be caused by atomic scattering vectors that happen to cancel each other out and are not related to systematic lattice parameters; these are not easily predictable and are called *accidental extinction*.

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[1] P = primitive lattice; C, B, A = side-centered on c-, b-, a-face; I = body centered; F = face centered (001)

(prepared by James R. Connolly, for EPS400-001, Introduction to X-Ray Powder Diffraction, Spring 2007)

Summary of Factors Affecting Relative Intensity of Bragg Reflections

By considering all of the factors affecting the relative intensity diffractions produced by the lattice planes of a crystal structure, it is possible to calculate a theoretical diffraction pattern for virtually any crystalline material. The ICDD 2006 PDF-4+ database contains almost 60,000 patterns calculated based on these factors, and the Inorganic Crystal Structure Database (ICSD) includes the calculated patterns and all of the detailed crystal structure data that can be used as a starting point for detailed pattern refinements done on experimental data. We will not actually do these calculations, but it is important to be aware of these factors when you interpret your data. They are summarized in the following sections.

Multiplicity of Bragg Planes

The number of identically spaced planes cutting a unit cell in a particular *hkl* family is called the plane *multiplicity factor*. For low symmetry systems, the multiplicity factor will always be low. For high symmetry systems, a single family of planes may be duplicated many times by symmetry operations, and each "duplicate" will add to the intensity of the diffraction. As an example, each cubic crystal face has a diagonal (110) and an equivalent ($\bar{1}$10) plane. With six faces, there are 12 crystallographic orientations. The (100) will similarly have 6 orientations. Thus, the (110) family will have twice the intensity of the (100) family because of the multiplicity factor.

Multiplicity factors for the various crystal classes and planes are given in Table 3.3 (from Jenkins and Snyder, 1996) below:

Table 3.3. Plane Multiplicity Factors, M_{hkl}

System	hkl	hhl	hh0	0kk	hhh	hk0	h0l	0kl	h00	0k0	00l
Cubic	48[a]	24	12	(12)	8	24[a]	(24[a])	(24[a])	6	(6)	(6)
Tetragonal	16[a]	8	4	(8)	(8)	8[a]	8	(8)	4	(4)	2
Hexagonal	24[a]	12[a]	6	(12)	(12)	12[a]	(12[a])	12[a]	6	(6)	2
Orthorhombic	8	(8)	(8)	(8)	(8)	4	(4)	(4)	2	(2)	(2)
Monoclinic	4	(4)	(4)	(4)	(4)	(4)	2	(4)	2	(2)	(2)
Triclinic	2	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)

[a] When all permutations of indices do not produce equivalent planes, *M* must be reduced by half.

The Lorentz Factor

When each lattice point on the reciprocal lattice intersects the diffractometer circle, a diffraction related to the plane represented will occur. The diffractometer typically moves at a constant 2θ rate, the amount of time each point is in the diffracting condition will be a function of the diffraction angle. As angles increase, the intersection approaches a tangent to the circle; thus at higher angles, more time is spent in the diffracting condition. This may be corrected by inserting the term $I/(\sin^2\theta \cos\theta)$ into the expression for calculating diffraction intensities; this is called the Lorentz factor. In practice, this is usually combined with the atomic scattering polarization term (Thompson equation) and called the Lorentz polarization (Lp) correction.

Extinction

In addition to systematic extinctions related to crystal structure, another extinction phenomenon can occur which is related to a phase-shifted reflection which can occur from the underside of very strongly reflecting planes. Directed towards the incident beam but

always 180° out of phase with it, the net effect is to reduce the intensity of the incident beam, and secondarily the intensity of the diffraction from that plane.

A similar phenomenon will reduce the penetration of the beam into strongly diffracting planes by reducing the primary beam energy which is redirected into the diffracted beam.

Corrections have been devised that require knowledge of the diffraction domain size, but this is very difficult to ascertain. Usually attempts to reduce this effect by thermally shocking the sample, inducing strains that reduce or eliminate the effect. The simplest way to reduce this effect is to make sure that particle size is uniformly fine. The effect will be reduced in samples in which the sizes of diffracting crystallites are consistently less than 1 μm, however this effect can still reduce the experimental intensities of the strongest reflecting peaks by up to 25%.

Absorption

Absorption phenomena related to fluorescence effects have already been discussed. Absorption also occurs related to the area of a powder specimen and depth of penetration of the x-ray beam into the specimen. In general, with a Bragg-Brentano diffractometer, the larger area of sample irradiated at low 2θ values have less depth of penetration. At higher 2θ values, the irradiated area will smaller, but depth of penetration greater. In general, these tend to be offsetting effects as related to diffracted intensity over the angular range of the data collection. The calculated intensity will include a term for $1/\mu_s$ where μ_s is the linear absorption coefficient of the specimen.

Microabsorption

Microabsorption is a phenomenon that occurs in polyphase samples. Typically the linear absorption coefficient is calculated based the proportions of the phases in the mixture. Microabsorption occurs when large crystals preferentially interact with the beam causing both anomalous absorption and intensities not representative of the proportions of the phases. The effect is minimized in diffraction experiments by decreasing the crystallite size in the specimen.

Monochromator Polarization

As noted previously, the diffracted beam is partially polarized by the diffraction process. A crystal monochromator can modify the intensity of the diffracted beam, thus a term related to the diffraction angle of the monochromator (θ_m) is added to the (Lp) correction. It should be noted that for pyrolitic graphite (PG) monochromators, the curved crystal geometry tends to minimize the intensity loss due to the polarization effect such that the correction term tends to over estimate the intensity loss.

The Intensity Equation

All of the previous factors affecting the intensity of a diffraction peak may be summarized in the following equations. Though we will not actually calculate diffraction patterns with these equations in this course, it can be done and is done regularly to produce the "calculated patterns" in the ICDD Powder Diffraction File database. This section is directly extracted from Jenkins and Snyder (1996).

Diffraction Basics, Part 2

The Intensity of diffraction peak from a flat rectangular sample of phase α in a diffractometer with a fixed receiving slit (neglecting air absorption), may be described as:

$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} v_\alpha}{\mu_s}$$

Here K_e is a constant for a particular experimental system:

$$K_e = \frac{I_o \lambda^3}{64\pi r}\left(\frac{e^2}{m_e c^2}\right)^2$$

where:

- I_0 = incident beam intensity
- r = distance from the specimen to the detector
- λ = wavelength of the X-radiation
- $(e^2/m_e c^2)^2$ is the square of the classical electron radius
- μ_s = linear attenuation coefficient of the specimen
- v_α = volume fraction of phase α in specimen

Also, $K_{(hkl)\alpha}$ is a constant for each diffraction reflection hkl from the crystal structure of phase α:

$$K_{(hkl)\alpha} = \frac{M_{hkl}}{V_\alpha^2}\left|F_{(hkl)\alpha}\right|^2 \left(\frac{1 + \cos^2(2\theta)\cos^2(2\theta_m)}{\sin^2\theta\cos\theta}\right)_{hkl}$$

where:

- M_{hkl} = multiplicity for reflection hkl of phase α
- V_α = volume of the unit cell of phase α
- the fraction in parentheses equals the Lorentz and polarization corrections for the diffractometer $(Lp)_{hkl}$, including a correction for the diffracted beam monochromator
- $2\theta_m$ = the diffraction angle of the monochromator
- $F_{(hkl)\alpha}$ = the structure factor for reflection hkl including anomalous scattering and temperature effects

Chapter 3 of Jenkins and Snyder (1996) includes a sample calculation of a diffraction pattern for potassium chloride (KCl). Students are encourage read the chapter and follow the procedures used in these calculations. This simple cubic example with two elements in the unit cell can be handled with relatively simple calculations. More complex diffraction pattern calculations are done with computers and programs specifically written for the purpose.

Anisotropic Distortions of the Diffraction Pattern

The figure at below (from Jenkins and Snyder, 1996) schematically illustrates the progression from atoms to crystalline structure.

A *crystallite* comprises a number of cells systematically grouped together to form a coherently diffracting domain. If the cells are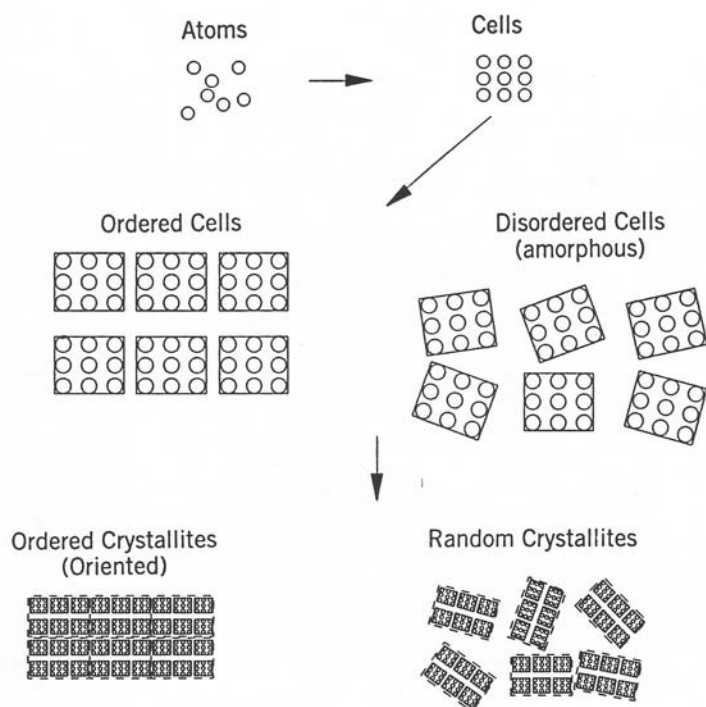 not identical, and show variations in atomic position destroying long range order, the material is *amorphous*. Where individual cells are highly ordered, the material is called *crystalline*. The "ideal" situation is that the individual crystallites in the sample are completely random. When the crystallites take up some common orientation, the specimen is showing *preferred orientation*.

In general, the most desirable analytical situation in a specimen is to have completely random orientation of uniformly small crystallites which possess sufficient long range order such that each crystallite diffracts strongly. Some types of diffraction analysis (i.e., the study of clay minerals) make use of preferred orientation of these crystallites, and in other types of analysis (i.e., qualitative phase identification) preferred orientation can be recognized and worked around to yield useful results in spite of it.

Figure 3.20. The structural makeup of solids.

Preferred Orientation

Many natural and engineered materials exhibit preferred orientation as a characteristic property of the material. Some types of ceramic magnets, extruded wires, most pressed powders and many engineered films and polymers require manipulating and measuring preferred orientation. This frequently involves the use of a special pole-figure diffractometer to measure a particular single diffraction.

In general powder diffraction data, preferred orientation is probably the most common cause of deviation of experimental diffractometer data from the ideal intensity pattern for the phase(s) analyzed. Preferred orientation can be recognized and compensated for when identifying crystalline phases in a specimen, but is much more difficult to deal with when attempting to do quantitative analysis or precise unit cell calculations.

The most common way of dealing with preferred orientation in a material of known composition is to compare the diffraction intensities of the specimen showing preferred

orientation with the calculated (random) pattern for the material. Some data analysis software (including MDI's Jade) will adjust data to correct for preferred orientation in a specimen when attempting quantitative analysis.

Crystallite Size

For large crystallites (i.e., thousands of unit cells), diffraction will result in "sharp" diffraction peaks only at the precise location of the Bragg angle. If the particle size is smaller (such that there are insufficient lattice planes to effectively cancel all incoherent scattering at angles close to the Bragg angle) the net result will be a broadening of the diffraction peak around the Bragg angle. This phenomenon of widening of diffraction peaks is related to incomplete "canceling" of small deviations from the Bragg angle in small crystallites is known as *particle size broadening*. Particle size broadening is differentiated from the normal width of diffraction peaks related to instrumental effects. In most cases, particle size broadening will not be observed with crystallite sizes larger than 1 μm. The crystallite size broadening (β_τ) of a peak can usually be related to the mean crystallite dimension (τ) by the Scherrer equation:

$$\tau = \frac{K\lambda}{\beta_\tau \cos\theta}$$

where β_τ is the line broadening due to the effect of small crystallites. Here β_τ is given by ($B - b$), B being the breadth of the observed diffraction line at its half-intensity maximum, and b the instrumental broadening or breadth of a peak that exhibits no 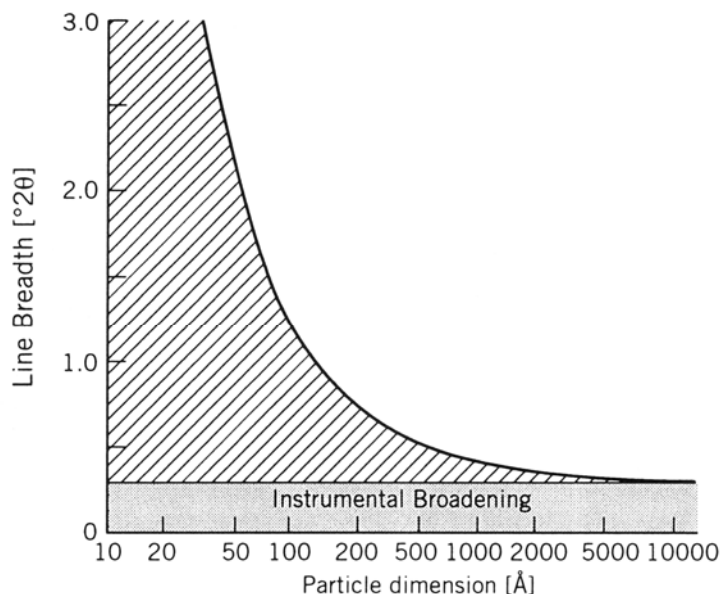broadening beyond the inherent instrumental peak width. Note that β_τ is given in radians, and that K is the shape factor which typically has a value of about 0.9. The general relation is shown in Fig. 3.21 (Jenkins and Snyder, 1996).

Note that particle size broadening is not significant at sizes above 10,000 Å (1 μm). When instrumental parameters are known (i.e., FWHM values for crystallites larger than 1 μm), the relationship above may be used to calculate crystallite sizes as small as 10 Å if the structures are unstrained.

Figure 3.21. Line width as a function of particle dimension.

It is interesting to think of particle size broadening when considering the diffraction pattern obtained from many amorphous materials. Typically these materials (like glass and plastics) will give an extremely broad peak over an angular range of perhaps 10° 2θ that will look like a "hump" in

the background. One can think of this "hump" as an extreme example of particle size broadening where the short range ordering is on the order of a several angstroms.

Residual Stress and Strain

Strain in a material can produce two types of diffraction effects. If the strain is uniform (either tensile or compressive) it is called *macrostrain* and the unit cell distances will become either larger or smaller resulting in a shift in the diffraction peaks in the pattern. Macrostrain causes the lattice parameters to change in a permanent (but possibly reversible) manner resulting in a peak shift. Macrostrains may be induced by glycolation or heating of clay minerals.

Microstrains are produced by a distribution of tensile and compressive forces resulting in a broadening of the diffraction peaks. In some cases, some peak asymmetry may be the result of microstrain. Microstress in crystallites may come from dislocations, vacancies, shear planes, etc; the effect will generally be a distribution of peaks around the unstressed peak location, and a crude broadening of the peak in the resultant pattern. These effects are shown in a very generalized way in Figure 3.23 (Jenkins and Snyder, 1996).
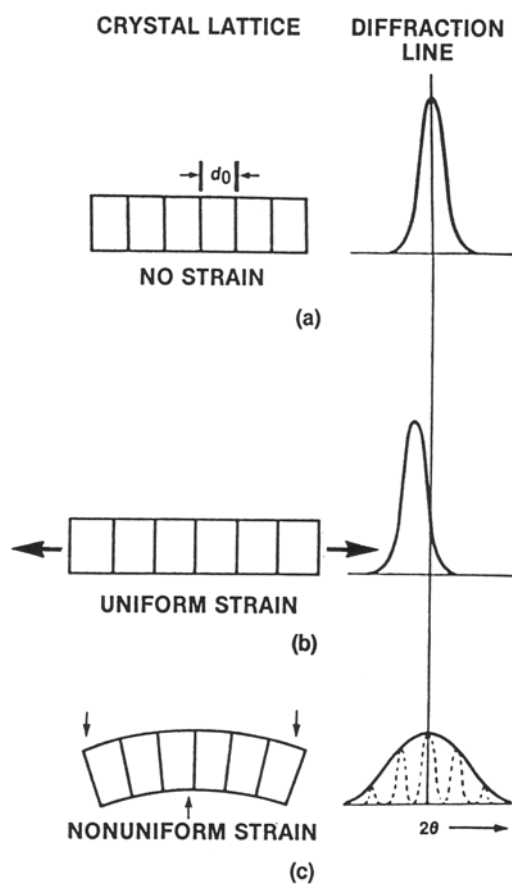
Figure 3.23. Strain expanding and contracting *d*-values.

Conclusions

This concludes our "theoretical" treatment of the diffraction process, including our crystallography review, and aspects of the crystal structure (peak positions) determination and crystal chemistry determination (intensities). In the next several weeks we will discuss the practical aspects of x-ray powder diffraction, and hopefully you will find that the theory lurking in the background of your data interpretations will assist greatly in helping to understand what your data is telling you.